Conducting Barrier Electrodes for Direct Contact of PZT Thin Films on Tungsten

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Abstract

Two W protection schemes for direct-contact bottom electrodes for PZT thin films, namely RuO_2 / Cr and RuO_2 / Ru, were compared with respect to protective performance and contact resistance up to 800°C annealing temperature in oxygen. Cr clearly offers better protection for W than Ru-based schemes by forming a passivating Cr_2O_3 layer. No Cr is detected on the RuO_2 surface, even after annealing at 800°C, due to its entrapment by RuO_2 by oxidoreduction. However, the formation of a continuous Cr_2O_3 film at the RuO_2 / Cr interface gives rise to an increased contact resistance above 650 °C. RuO_2 / Ru does not show any measurable contact resistance on W, but fails above 600°C.

1. Introduction

Thin films of PZT and other similar ferroelectrics are generating considerable interest, due to their possible applications in piezoelectric sensors and actuators [1], infrared detectors [2] and memories [3], offering superior performance to non-ferroelectrics.

The main problem is the integration of high quality PZT films on the desired substrates and suitable bottom electrodes. The required oxidizing atmosphere at 550 to 700°C and the high diffusivity of lead potentially degrade the bottom electrode / substrate structure and reduce the quality of the PZT films. Direct deposition on reactive metals is therefore impossible [4].

The most widely used substrate is silicon, which is ideal for integration purposes. Thermal or high quality CVD silicon oxide or nitride passivate silicon against oxidation, and a platinum or conducting oxide (often RuO_2) film serves as the bottom electrode and lead diffusion barrier. While adequate for many purposes, this scheme presents a number of problems. First, via fabrication through the Si oxide/nitride after PZT deposition is needed, which is a serious contamination problem. Second, vias waste considerable space in memory applications, where highest density is required. Last, deposition on simpler and less brittle substrates, such as metals, provides an interesting alternative for piezoelectric devices, especially since micromachining can be avoided by using thin metallic sheets. Therefore, a conductive oxidation barrier - electrode combination is desired, maintaining electric contact between the PZT and the substrate, obviating the need for via fabrication on silicon and allowing deposition on metallic substrates. Candidate metals are sheets of materials like stainless steel, Ti and Zr for membrane applications. For micro-electronic devices, materials needing protection are typically refractive barrier metals or compounds such as TiN, TiW and W. Previous work [5] for memory applications used a Pt / RuPt alloy / W plug on silicon. In a previous paper [6], we demonstrated PZT deposition on a very reactive metal (Zr), using a RuO_2 / Cr metal combination. The same bilayer was found to work on Si [7] using an additional TiN or TiW barrier layer between Si and Cr, tough we did not characterize contact resistance. This work aims to compare the protective character and contact resistance of a reactive metal (Cr) with that of noble metals (Ru, Pt) for the protection of W. Evolution of contact resistance was measured between the metal layers and a RuO_2 bottom electrode. RuO_2

is preferable to noble metals such as Pt or Ru in this case as it "traps" out-diffusing reactive metals, preventing their diffusion into PZT [6].

2. Experimental

The sample films were deposited using a Nordiko 2000 sputtering system on SiO_2 (1 μm) / Si substrates. The metal / electrode sequences were put down at 500°C, in order to ensure dense, high quality films. Thin (typically 10 nm) Ti adhesion layers were used on SiO_2 and for RuO_2 on Cr.

Two types of measurements were done: oxidation resistance and contact resistance. The former shows the global oxidation resistance of a stack, while the latter characterizes the possible formation of intermediate insulating layers inside the electrode. The degradation of the samples was mainly assessed electrically by measuring the evolution of electric resistance along the film (oxidation resistance), and at an interface (contact resistance).

For oxidation resistance measurements, a “line” of film (typically 3-5 mm wide) was deposited between two thick (500 nm) Ru pads (fig. 1a), allowing determination of electrical resistance using a 4 wire method. In the contact resistance measurement configuration (fig. 1b), a line of the bottom film is put down, then a line of the top film is deposited perpendicular to it, forming a cross. A 4 wire method is also used, eliminating the effect of the electrical resistance of the cross legs.

The samples are listed in tables 1 (oxidation resistance), and 2 (contact resistance). Both types of samples were subjected to cumulative oxidation tests of 10 minutes duration at 200, 300, 400, 450, 500, 550, 600, 650, 700, 750 and 800°C in 1 atm oxygen. Degradation was assessed by change of the electrical resistivity and thickness, which were measured ex situ between each oxidation. Thickness measurements were made using an alpha step profilometer. Also, film integrity was assessed optically and, in the case of the RuO_2 / Cr interface, by transmission electron microscopy (TEM).

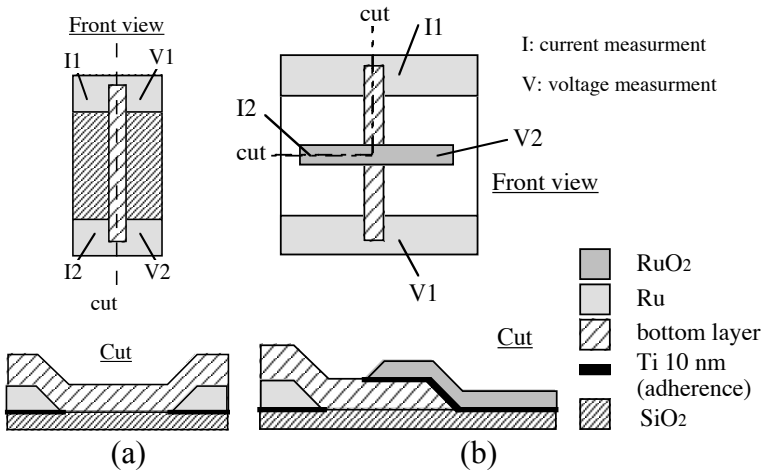

Figure 1. Samples for measurement of electrical resistance along the film (a) and contact resistance (b).

Sequences (Ti: thin adhesion layer)	**Thicknesses [nm]**
Pt / (Ti) / W / (Ti)	250 / (10) / 540 / (20)
Ru / W / (Ti)	250 / (10) / 550 / (20)
RuO_2 / Ru / (Ti) / W / (Ti)	300 / 150 / (10) / 430 / (10)
Cr / W / (Ti)	270 / (10) / 640 / (20)
Cr / W / (Ti)	500 / (10) / 520 / (20)
W / (Ti) - reference	400 / (10)

Table 1. List of samples for oxidation measurements.

Sequences (top x bottom leg)	**Thicknesses [nm]**
RuO_2 / (Ti) × Ru / W / (Ti)	300 / (10) x 150 / 430 / (10)
RuO_2 / (Ti) × Cr / (Ti)	300 / (10) x 500 / (10)

Table 2. Samples for contact resistance measurements.

3. Results

Oxidation resistance

The relative conductance (conductance of the sample relative to as-deposited) of the samples is given in fig. 2, as a function of (cumulative) anneal temperature. Compared to the catastrophic oxidation of W, all protection schemes show an improvement. However, schemes based on noble metals (Pt, Ru, RuO_2 / Ru) fail above 600-650°C. Beyond, extensive delamination, especially at the protective layer / W interface, is observed. We used both RuO_2 / Ru and Ru, because the Ru surface was found to oxidize in a very irregular fashion. Obviously, the RuO_2 nucleates but with difficulty under these conditions. This problem was solved by adding a RuO_2 film on top of the Ru, giving the RuO_2 / Ru sequence.

On the other hand, Cr is very effective at protecting the W film up to 800°C, forming a layer of Cr_2O_3 on the sample surface. While conductivity does eventually drop by oxidation, no delamination is observed.

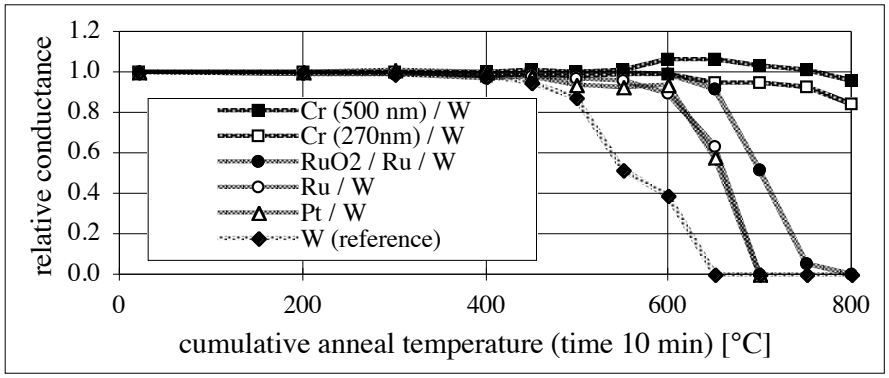

Figure 2. Relative conductance as a function of cumulative anneal temperature for various W protection schemes.

Contact resistance

The contact resistance of the two samples are shown in fig. 3. RuO_2 × Ru / W keeps a low contact resistance, but the bottom Ru / W leg delaminates at 650°C (as in the previous experiment), RuO_2 × Cr has a slight contact resistance in the as-deposited state. As the sample starts to react (550-650°C), the resistance actually drops, than increases again beyond to high values. However, the sample does not delaminate or structurally fail in any way up to 800°C.

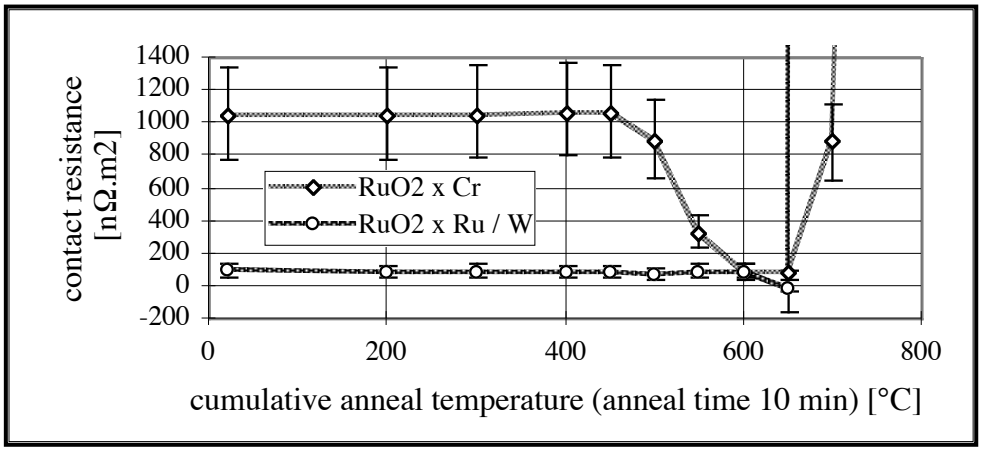

Figure 3. Evolution of contact resistance between the RuO_2 electrode and the bottom layers as a function of cumulative anneal temperature.

TEM Observations

The RuO_2 / Cr interface was observed after the tests (all anneals up to 800°C). The corresponding TEM cross-section are shown in fig. 4. A thick layer of Cr_2O_3 has formed at the RuO_2 / Cr interface. No Cr_2O_3 is seen at the top of the RuO_2, which confirms at much higher temperatures our previous results that RuO_2 is an outstanding barrier to Cr out-diffusion [6, 7].

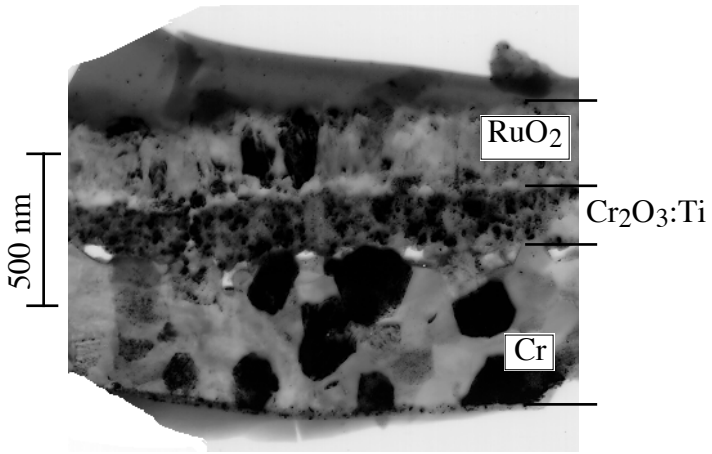

Figure 4. TEM cross-section of the RuO_2 / Cr sequence after (10) min at 800°C in oxygen.

4. Discussions

Protection performance

Barriers based on noble metals, as in the case of Ru / W and Pt / W, have limited performance, as the preferential oxidation of the most reactive metal (W) provides a driving force for oxygen and/or reactive metal diffusion across the noble metal, leading to ultimate failure. The same mechanisms contribute to the rapid oxidation and diffusion of the Ti adhesion layers used for Pt electrodes on passivated silicon [8, 9, 10, 11, 12]. On the other hand, when the protective metal is the more reactive (Cr / W), it oxidizes preferentially [13]. In our case, a protective Cr_2O_3 scale develops, preventing the oxidation of W, even if some W has reached the Cr surface by metal - metal diffusion. The higher reactivity of Cr also prevents oxidation of W below Cr.

Since Cr is much more reactive than Ru, it will oxidize on contact with RuO_2, according to the following oxidoreduction reaction:

$$4Cr + 3RuO_2 \rightarrow 2Cr_2O_3 + 3Ru.$$

The RuO_2 / Cr interface is therefore inherently unstable thermodynamically. Depending on the availability of oxygen diffusing through the RuO_2, Ru will stay metallic or oxidize again to RuO_2. In any case, the Cr is oxidized at the bottom of the RuO_2, which considerably lowers its driving force for diffusion to the surface. Our results show this trapping mechanism is very efficient up to 800°C, way above the processing temperatures used in PZT fabrication. Cr diffusion into PZT is therefore not a concern.

Also, the wide oxygen pressure stability domain of Cr_2O_3 allows the use of this barrier type with any deposition method (sputtering, sol-gel, MOCVD, etc.). Moreover, the harsh anneal schedule used, i.e. cumulative anneals and thermal cycling between room and anneal temperature, prove that the barrier is quite robust.

Contact resistance

The formation of a thick Cr_2O_3 layer between Cr and RuO_2 eventually gives rise to an increased contact resistance. However, the contact resistance first drops up to 600°C. Therefore, three stages of interface evolution are thought to occur:

1) The Cr surface is initially oxidized due to the reactive plasma used during RuO_2 deposition. Also, the TiO_2 layer formed by oxidation of the Ti adhesion layer (during the same RuO_2 deposition) may contribute to the contact resistance.
2) The contact resistance is first reduced in the 400-600°C temperature range by oxidoreduction or intermixing of Cr_2O_3, TiO_2 and RuO_2. Obviously, this means that the oxygen from the atmosphere does not diffuse through the RuO_2.
3) At higher temperatures, the $RuO_2$is no longer a barrier against oxygen diffusion, and oxidation gives rise to a thick, insulating layer of Cr_2O_3.

Below 650°C, the measured contact resistance is low enough for piezoelectric devices after a special anneal, which can coincide with PZT deposition. However, for memory applications, more sensitive measurement techniques and layouts are needed in order to judge the performance.

5. Conclusions

In conclusion, an electrically conductive buffer layer scheme for PZT deposition on reactive metal substrates was developed and successfully tested. Diffusion and chemical reactions are limited to the RuO_2 / Cr interface, with no Cr diffusion through RuO_2 up to 800°C. The contact resistance is low enough for high-frequency piezoelectric applications. This barrier scheme may be potentially applied in memories.

6. Acknowledgments

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7. Bibliography

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